Preparation of Polyvinylamine/Polysulfone Composite Hollow-Fiber Membranes and Their CO_2/CH_4 Separation Performance

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ABSTRACT: Fixed-carrier composite hollow-fiber membranes were prepared with polyvinylamine (PVAm) as the selective layer and a polysulfone ultrafiltration membrane as the substrate. The effects of the PVAm concentration in the coating solution, the number of coatings, and the crosslinking of glutaraldehyde and sulfuric acid on the CO_2 permeation rate and CO_2/CH_4 selectivity of the composite membranes were investigated. As the PVAm concentration and the number of coatings increased, the CO_2/CH_4 selectivity increased, but the CO_2 permeation rate decreased. The membranes crosslinked by glutaraldehyde or sulfuric acid possessed higher CO_2/CH_4 selectivities but lower CO_2 permeation rates. For the pure feed gas, a composite hollow-fiber membrane coated with a 2 wt % PVAm solution two times and then crosslinked with glutaraldehyde and an acid solution in sequence had a CO_2 permeation rate of 3.99×10^{-6} cm^3 cm^{-2} s^{-1} $cmHg^{-1}$ and an ideal CO_2/CH_4 selectivity of 206 at a feed gas pressure of 96 cmHg and 298 K. The effect of time on the performance of the membranes was also investigated. The performance stability of the membranes was good during 6 days of testing. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1885–1891, 2006

Key words: composites; fibers; membranes

INTRODUCTION

Cryogenic distillation, pressure swing adsorption, and membrane technology are the main means of gas separation. Among these means, membrane separation processes offer a number of advantages in terms of no phase changes and low energy use. The processes require simple, compact equipment, and the equipment is easy to operate. As a result, the processes have become very important subjects in gas separation.[1–4] Membrane technology used for CO_2 separation has wide uses in many fields, such as the purification of natural gas, the relief of global warming, the recovery of carbon resources, and the recycling of air in limited living spaces.

There have been many studies on membrane technology for CO_2 separation. Cellulose acetate and polysulfone (PS) membranes have been used in some areas. They have higher selectivity and lower permeability.[3] Polyimide membranes have attracted much attention,[5,6] but their performance is similar to that of cellulose acetate and PS membranes. On the contrary, other polymeric membranes such as poly(trimethylsilyl propyne) and poly(methylsilylmethyl methacrylate) membranes have higher permeability and lower selectivity.[7,8] Fixed-carrier membranes are new membranes that have the advantages of both supported liquid membranes and polymeric membranes by fixing active carriers to polymer chains. Yoshikawa and coworkers[9,10] investigated the permeation of CO_2 with synthetic polymer membranes having a pyridine moiety and found that the amine group could facilitate the transport of CO_2. Matsuyama and coworkers[11,12] also found that the amine group could act as an active carrier. In previous work,[13] we studied the performance of composite membranes with poly(N-vinyl-γ-sodium aminobutyrate) as a selective layer and found that the carboxylic acid ion could also facilitate the transport of CO_2. Until now, all the fixed-carrier membranes for CO_2 separation reported in the literature have been flat membranes.

In this work, a novel water-soluble material, polyvinylamine (PVAm), was obtained through Hoffmann degradation of polyacrylamide (PAM). It consisted of amine and carboxylic acid groups that can act as active carriers of CO_2. Composite hollow-fiber membranes were prepared with PVAm as the selective layer and a PS ultrafiltration membrane as the substrate. The main goal of this study was to investigate the effects of various parameters in the membrane preparation pro-
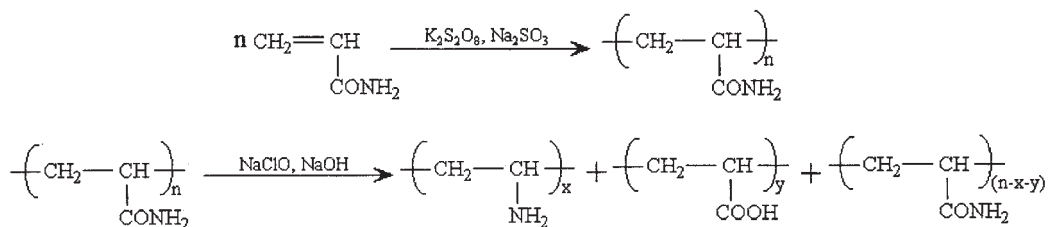
Figure 1 Reaction scheme of the synthesis of PVAm ($x = 70–80\%$, $y = 15–20\%$).

cesses on the CO_2/CH_4 separation performance of the composite hollow-fiber membranes. The synthesis of PVAm and the mechanism of the facilitated transport will be discussed in detail in future publications.

EXPERIMENTAL

Materials

Polyacrylamide was synthesized through radical polymerization in a 10 wt % acrylamide aqueous solution with ammonium persulfate as the initiator at 49°C in an inert atmosphere of nitrogen gas. PVAm, which contains major amine and minor amide and carboxylic acid groups, was obtained by Hoffmann degradation and purified by solution–precipitation method before being used. The reaction scheme of the synthesis of PVAm is shown in Figure 1.

Module fabrication

The PVAm/PS composite hollow-fiber membranes were prepared by the dipping of a PS hollow-fiber membrane into a PVAm aqueous solution for a certain time (first coating time = 30 min; second coating time = 1 min; third coating time = 0.5 min) and drying in a clean atmosphere at room temperature. The PS hollow-fiber membrane, with an average cutoff value of 5×10^4, was modified by being dipped into a sodium dodecyl sulfate aqueous solution (4 g/L) for 90 min at 60°C before being used. The crosslinked composite membranes were prepared by the dipping of the PVAm-coated PS hollow fibers into a crosslinking agent solution for a certain time (0.5 min in a glutaraldehyde aqueous solution and 2 min in a sulfuric acid aqueous solution) and drying in a clean atmosphere. Test modules consisting of a bundle of five 20-cm-long composite hollow fibers were constructed. The shell sides of the two ends of the bundle were glued in a poly(methyl methacrylate) tube with a standard epoxy resin.

Gas permeation test

The gas permeation of the membranes was measured with a test apparatus. The feed gas was a mixture of CO_2 and CH_4 or pure CO_2 and pure CH_4. Before the membrane was contacted, both the feed gas and the sweep gas (H_2, 0.08–0.1 mL/s) were passed through gas bubblers containing water. The outlet sweep gas

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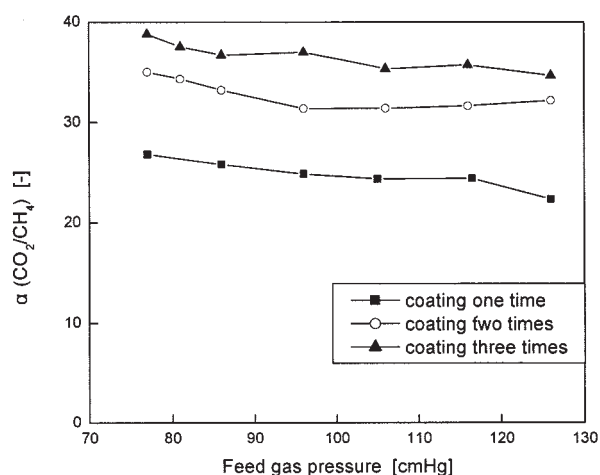

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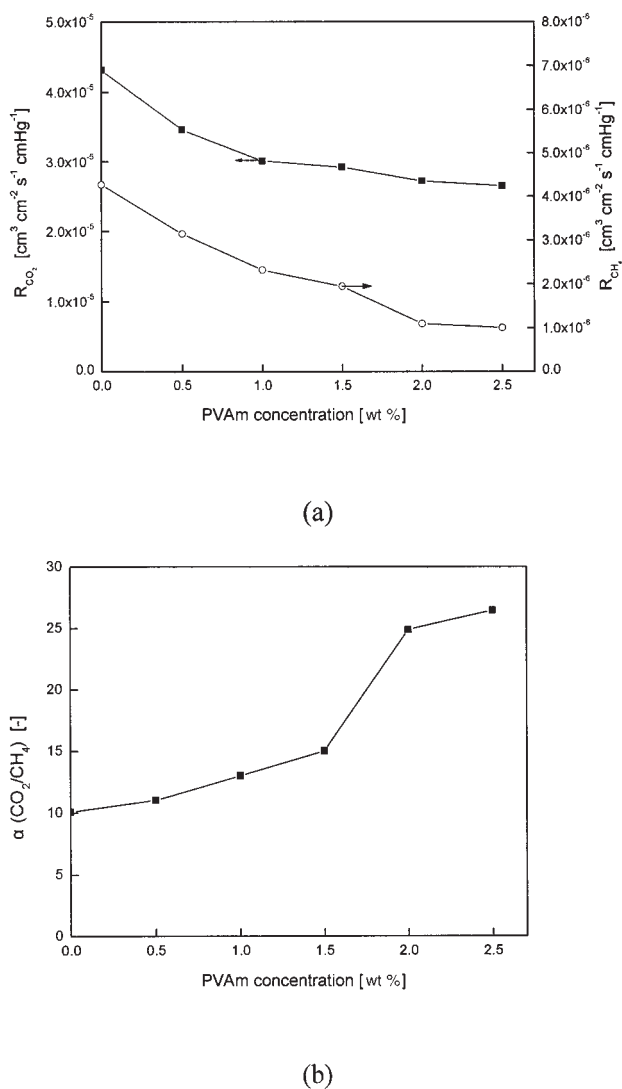
Figure 2 Effect of the PVAm concentration in the coating solution on (a) R_{CO2} and R_{CH4} and (b) $\alpha_{CO2/CH4}$ of PVAm/PS composite membranes (testing temperature = 298 K, feed gas pressure = 96 cmHg, feed gas = 50 vol % CO_2/50 vol % CH_4, number of coatings = 1).
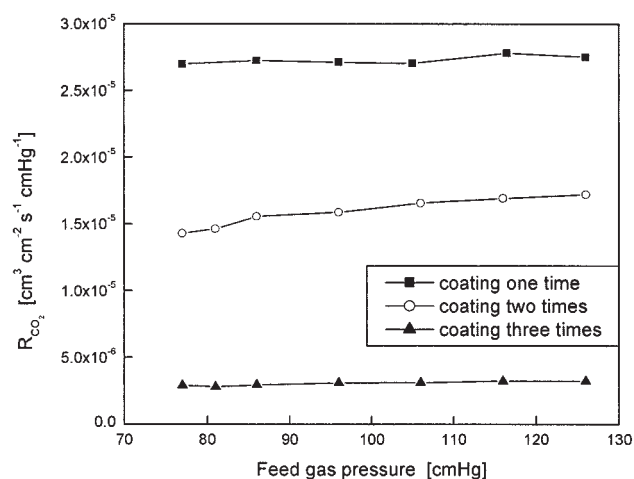
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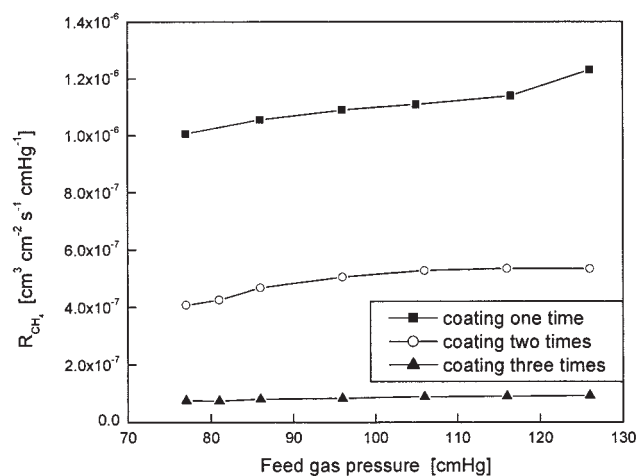
(b)

(c)

composition was analyzed by a gas chromatograph equipped with a thermal conductivity detector (HP4890, Porapak N; Agilent, Wilmington, DE). The fluxes of CO_2 (N_{CO2}) and CH_4 (N_{CH4}) were obtained from the sweep gas flow rate and its composition. The downstream pressure in the apparatus was 1 atm. The gas permeation rate (R_i) and the CO_2/CH_4 selectivity ($\alpha_{CO2/CH4}$) were calculated with $R_i = N_i/\Delta P_i$, where N_i is the flux and ΔP_i is the transmembrane pressure difference (cmHg), and with $\alpha_{CO2/CH4} = R_{CO2}/R_{CH4}$, where R_{CO2} is the CO_2 permeation rate and R_{CH4} is the CH_4 permeation rate.

RESULTS AND DISCUSSION

Effects of the PVAm concentration and number of coatings

Figure 2 shows the effect of the PVAm concentration in the coating solution on R_{CO2}, R_{CH4}, and $\alpha_{CO2/CH4}$ of PVAm/PS composite hollow-fiber membranes. Compared with that of the original PS hollow-fiber substrate (expressed as the zero point of the PVAm concentration in Fig. 2), R_{CO2} drops quickly at first and then drops slowly as the PVAm concentration increases. R_{CH4} gradually drops as the PVAm concentration increases when the PVAm solution concentration is no more than 2 wt %. $\alpha_{CO2/CH4}$ changes little at low PVAm concentrations ($\leqslant$1.5 wt %) and then significantly increases as the PVAm concentration increases. When the PVAm concentration is higher than 2 wt %, $\alpha_{CO2/CH4}$ changes little. An explanation for these results might be that when the PVAm concentration is low, the coated PVAm layer cannot completely cover the surface of the PS hollow fiber. There are still many defects on the skin, so $\alpha_{CO2/CH4}$ changes little. However, this coating layer increases the permeation resistance and thus decreases the gas permeation rate of the hollow fiber significantly. With increasing PVAm concentration, the coating layer thickness increases, and defects on it decrease. As a result, $\alpha_{CO2/CH4}$ improves dramatically. When the PVAm concentration reaches 2 wt %, the coated layer almost covers the whole surface of the substrate hollow fiber, and adding more PVAm does not significantly improve permselectivity of membrane. Thus, R_{CO2}, R_{CH4}, and $\alpha_{CO2/CH4}$ change little when the PVAm concentration in the coating solution is higher than 2 wt %.

The effect of the number of coatings on the gas-separation performance of the PVAm/PS composite

Figure 3 Effect of the number of PVAm coatings on (a) R_{CO2}, (b) R_{CH4}, and (c) $\alpha_{CO2/CH4}$ of PVAm/PS composite membranes (testing temperature = 298 K, feed gas = 50 vol % CO_2/50 vol % CH_4, PVAm concentration in the coating solution = 2 wt %).
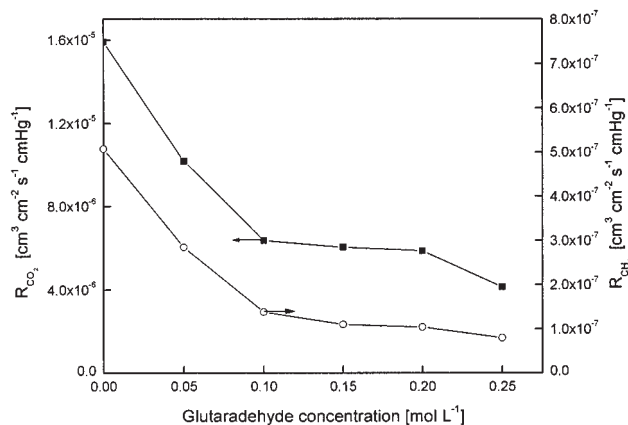
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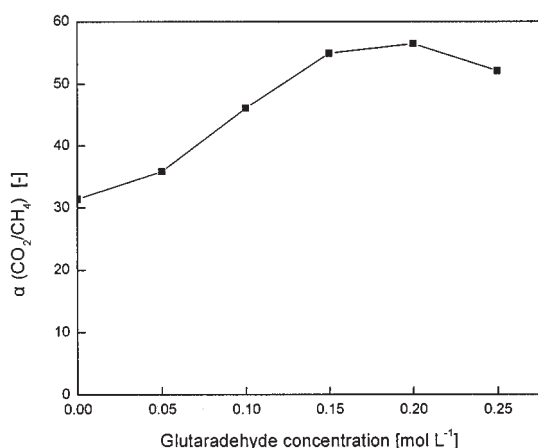
(b)

Figure 4 Effect of the glutaraldehyde concentration on (a) R_{CO2} and R_{CH4} and (b) $\alpha_{CO2/CH4}$ of PVAm/PS composite membranes (testing temperature = 298 K, feed gas = 50 vol % CO_2/50 vol % CH_4, feed gas pressure = 96 cmHg, number of coatings with a 2 wt % PVAm aqueous solution = 2, crosslinking time = 0.5 min).

hollow-fiber membranes is shown in Figure 3. R_{CO2} and R_{CH4} drop dramatically and $\alpha_{CO2/CH4}$ increases as the number of coatings increases. This is due to an increase in the permeation resistance and a decrease of

defects in selective layer. Figure 3 also shows that $\alpha_{CO2/CH4}$ has a large increase when there are two coatings. Because of these results, two coating steps were carried out in the following research.

Effects of crosslinking

Figure 4 shows the effect of glutaraldehyde crosslinking on the gas-separation performance of the composite membranes. R_{CO2} and R_{CH4} decrease when the composite membranes are crosslinked. $\alpha_{CO2/CH4}$ has a maximum with increasing glutaraldehyde concentration. The glutaraldehyde crosslinking, which has the mechanism shown in Figure 5, leads to two results. First, the crosslinkage reduces the mobility of the polymer, which leads to the decrease in R_{CO2} and R_{CH4}.[14] Second, the amine group concentration lessens because of the reaction between it and glutaraldehyde, and this decreases R_{CO2}. The superposition of these two results shows that at low glutaraldehyde concentrations (<0.2 mol/L), the selectivity increases with the glutaraldehyde concentration; but when the glutaraldehyde concentration is more than 0.2 mol/L, the selectivity decreases with the glutaraldehyde concentration.

The presence of hydronium ions can make the polymer become a stereoweb structure by hydrogen bonding with the amine and carboxylic acid groups. Therefore, the sulfuric acid crosslinking can also change the performance of the composite membranes. This result is shown in Table I. R_{CO2} and R_{CH4} decrease with an increase in the acid concentration. This is because the coating layer becomes denser with an increase in the acid concentration. The hydronium ion can also increase the polarity of the composite membranes and reduce the permeation rate of the nonpolar gas CH_4. As a result, $\alpha_{CO2/CH4}$ increases with increasing acid concentration. When the acid concentration is higher than 0.15 mol/L, however, carbonification can be found on the composite membranes. Thus, the appropriate acid concentration should be no more than 0.15 mol/L.
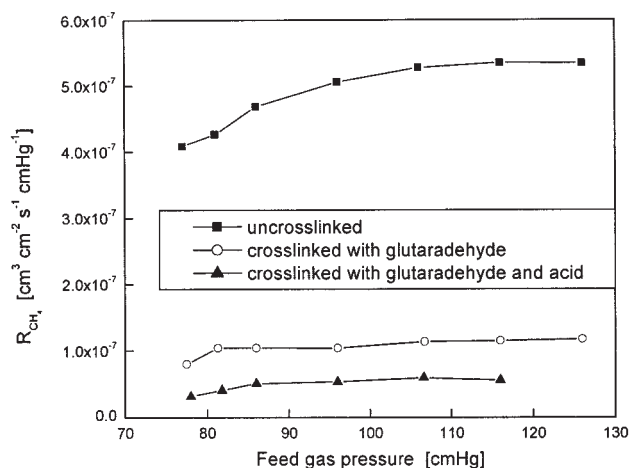
The uncrosslinked coating layer is easily swelled when it is exposed to humid gases, and when exposed for a long time or exposed to water, it will drop off easily. The crosslinked coating layer will also swell but
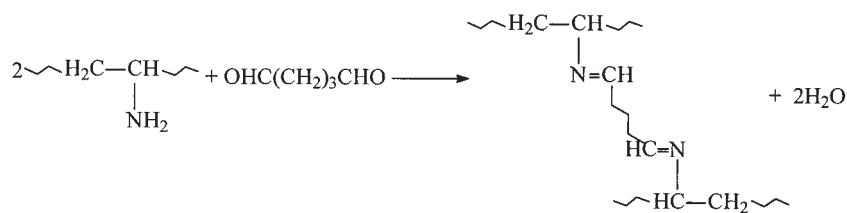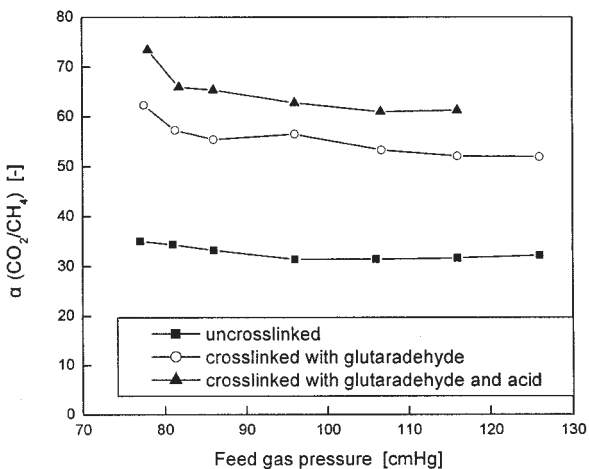

Figure 5 Reaction scheme of glutaraldehyde crosslinking.
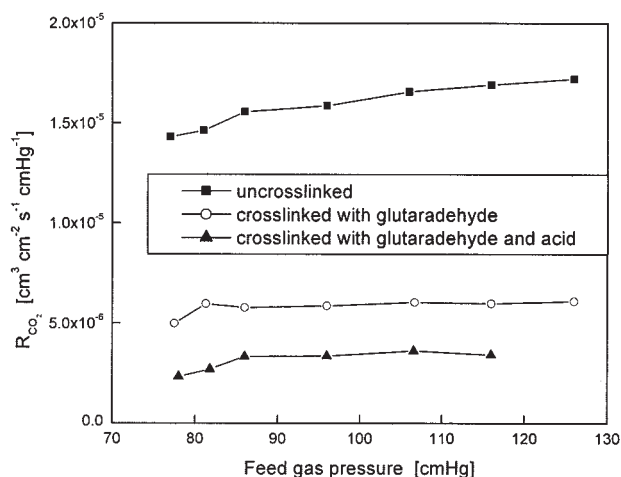
(a)

(b)

(c)

TABLE I
Effect of the Acid Concentration on the CO_2/CH_4 Separation Performance of the PVAm/PS Composite Membranes

Acid concentration (mol/L)	R_{CO2} (GPU)	R_{CH4} (GPU)	$\alpha_{CO2/CH4}$
0	15.90	0.506	31.4
0.05	10.81	0.317	34.1
0.1	8.19	0.217	37.8
0.15	7.16	0.182	39.3

Testing temperature = 298 K; feed gas = 50 vol % CO_2 + 50 vol % CH_4; feed gas pressure = 96 cmHg; Coating was done two times with a 2 wt % PVAm aqueous solution; Crosslinking was done with H_2SO_4 for 2 min; 1 GPU = 1 $\times$ 10^{-6} cm^3 cm^{-2} s^{-1} $cmHg^{-1}$.

never drop off even when exposed to water. This has been confirmed by our experiments. Both the glutaraldehyde crosslinking and the acid crosslinking make the coating layer more durable and denser. The difference is that the acid crosslinking is a kind of secondary bond crosslinking due to hydrogen bonding and does not consume the amine group, whereas the glutaraldehyde crosslinking is a covalent bond crosslinking of the amine group with glutaraldehyde and consumes the amine group. Moreover, it is difficult to control the degree of glutaraldehyde crosslinking when the glutaraldehyde concentration is high because that there are many factors, such as temperature and humidity, that can affect the crosslinking. Therefore, the composite membranes are expected to have better performance when crosslinked with glutaraldehyde and acid in a definite sequence. The permselectivities of the composite membranes, which are uncrosslinked, crosslinked with glutaraldehyde, and crosslinked first with glutaraldehyde and then with acid, are compared in Figure 6. The acid crosslinking increases the polarity and density of the glutaraldehyde-crosslinked composite membrane. Therefore, $\alpha_{CO2/CH4}$ becomes higher, but R_{CO2} and R_{CH4} decrease.

Coupling between the gas components

When the membrane performance with mixed feed gases is measured, there must be coupling between the gas components. The performance of the composite membrane crosslinked with glutaraldehyde and

Figure 6 Effects of glutaraldehyde and acid crosslinking on (a) R_{CO2}, (b) R_{CH4}, and (c) $\alpha_{CO2/CH4}$ of PVAm/PS composite membranes (testing temperature = 298 K, feed gas = 50 vol % CO_2/50 vol % CH_4, number of coatings = 2 with a 2 wt % PVAm aqueous solution, crosslinking time with a 0.2 mol/L glutaraldehyde aqueous solution = 0.5 min, crosslinking time with a 0.1 mol/L H_2SO_4 aqueous solution = 2 min).

acid measured with pure feed gases is shown in Figure 7. Figures 6 and 7 show that the membranes have higher R_{CO2} values and lower R_{CH4} values when pure feed gases are used, and therefore the ideal $\alpha_{CO2/CH4}$ value is much more than the real selectivity measured with mixed feed gases. This indicates that the interactions between CO_2, CH_4, and the membrane are quite strong. These interactions include the swelling and plasticization of the matrix by CO_2 and the diffusion competition of the two gas components. As a comprehensive result, the existence of CH_4 will decrease R_{CO2} because of the competition in the diffusion route, but the existence of CO_2 will increase R_{CH4} because of

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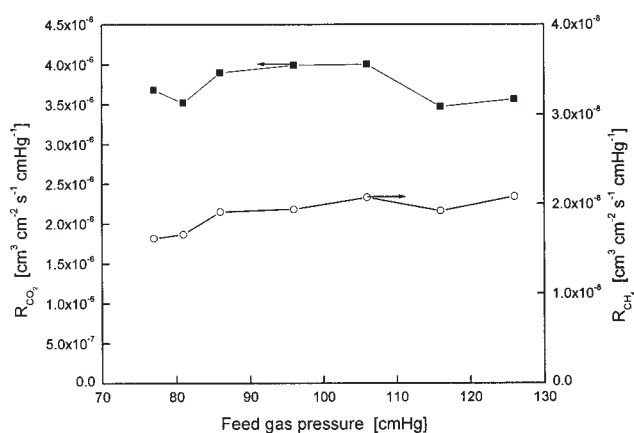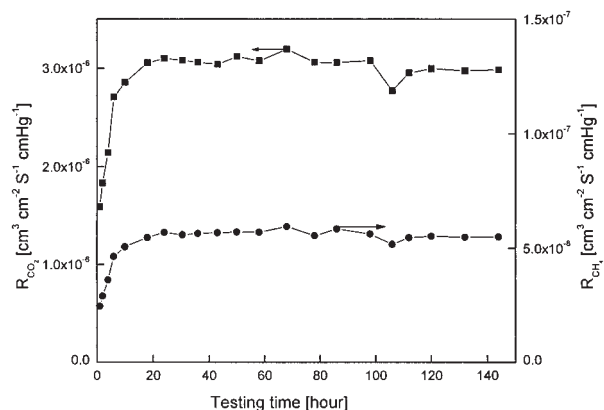

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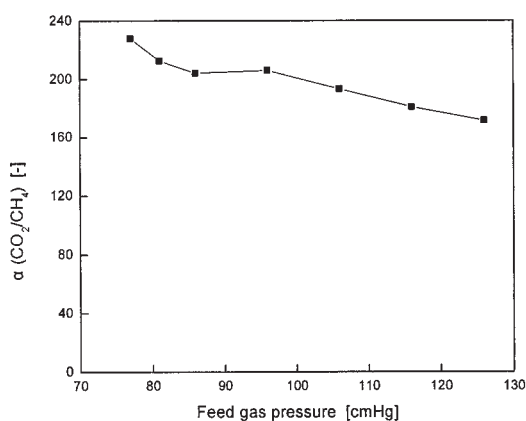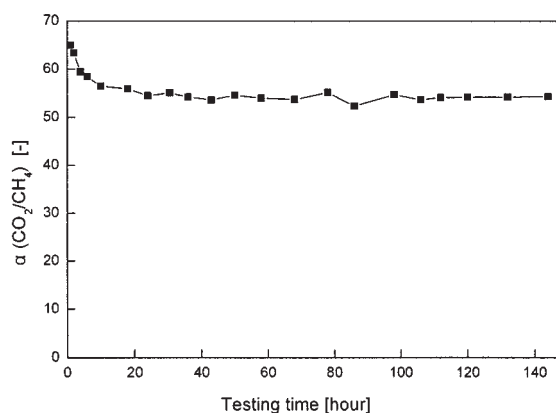

(b)

Figure 7 Performance of crosslinked PVAm/PS composite membranes for a pure feed gas: (a) R_{CO2} and R_{CH4} and (b) $\alpha_{CO2/CH4}$ (testing temperature = 298 K, number of coatings with a 2 wt % PVAm aqueous solution = 2, crosslinking time with a 0.2 mol/L glutaraldehyde aqueous solution = 0.5 min, subsequent crosslinking time with a 0.1 mol/L H_2SO_4 aqueous solution = 2 min).

(b)

Figure 8 Effect of the testing time on (a) R_{CO2} and R_{CH4} and (b) $\alpha_{CO2/CH4}$ of crosslinked PVAm/PS composite membranes (testing temperature = 298 K, feed gas pressure = 96 cmHg, feed gas = 50 vol % CO_2/50 vol % CH_4, number of coatings with a 2 wt % PVAm aqueous solution = 2, crosslinking time with a 0.2 mol/L glutaraldehyde aqueous solution = 0.5 min, subsequent crosslinking with a 0.1 mol/L H_2SO_4 aqueous solution = 2 min).

swelling and plasticization, and therefore the real $\alpha_{CO2/CH4}$ value is lower than the ideal $\alpha_{CO2/CH4}$ value.

Stability of the membrane performance

The effect of time on the gas-separation performance of a crosslinked composite membrane measured with a feed gas composed of 50 vol % CO_2 and 50 vol % CH_4 at the feed gas pressure of 96 cmHg and 298 K for 6 days is shown in Figure 8. $\alpha_{CO2/CH4}$ decreases at first and then almost remains constant. The gas permeation rate increases significantly at first and then changes little. This is because the feed gas was passed through gas bubblers containing water before it contacted the membrane. The composite membrane with a water-soluble coating layer will at first swell and then reach

a steady state. As the coating layer swells, N_{CO2} and N_{CH4} become higher, but $\alpha_{CO2/CH4}$ becomes lower. The steady-state R_{CO2} value was approximately 3.0×10^{-6} cm^3 cm^{-2} s^{-1} cmHg^{-1}, and the steady-state $\alpha_{CO2/CH4}$ value was approximately 53. This indicates that the performance of the crosslinked composite hollow-fiber membrane developed in this work is stable.

CONCLUSIONS

A novel water-soluble material, PVAm, that could facilitate the transport of CO_2 was synthesized. A fixed-carrier composite hollow-fiber membrane was prepared for the first time with PVAm as the selective layer and a PS ultrafiltration membrane as the substrate.

A composite membrane with an almost defect-free coated layer was made when the PVAm coating solution concentration was 2 wt % and the number of coatings was two. $\alpha_{CO2/CH4}$ of the composite membrane was improved by crosslinking with glutaraldehyde and a sulfuric acid aqueous solution. Furthermore, the composite membrane crosslinked with glutaraldehyde and acid in sequence exhibited an excellent performance. The ideal $\alpha_{CO2/CH4}$ value was 206, and the permeation rate of pure CO_2 was 3.99×10^{-6} cm^3 cm^{-2} s^{-1} cmHg^{-1} at a feed gas pressure of 96 cmHg and 298 K.

The performance stability of the composite hollow-fiber membrane was good during 6 days of testing with a feed gas composed of 50 vol % CO_2 and 50 vol % CH_4 at a feed gas pressure of 96 cmHg and 298 K. The steady-state R_{CO2} value was approximately 3.0×10^{-6} cm^3 cm^{-2} s^{-1} cmHg^{-1}, and the steady-state $\alpha_{CO2/CH4}$ value was approximately 53.

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